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SCALING LAWS AND MESOSCOPIC MODELING OF HEAT TRANSFER IN NANOFIBROUS MATERIALS AND COMPOSITES

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14. ABSTRACT

The structure – thermal transport properties relationship for nanofibrous materials based on carbon nanotubes (CNTs) are investigated by performing a multiscale computational study combining atomistic molecular dynamics simulations of heat transfer in small groups of CNTs with mesoscopic modeling of thermal conductivity in CNT-based materials, such as CNT bundles, "buckypaper," and vertically-aligned CNT "forests." Some of the key results of this study are as follows. (1) General scaling laws governing the heat transfer in nanofibrous network materials with different structural organization are derived analytically and verified in mesoscopic simulations; (2) Contrary to the common assumption of the dominant effect of the contact CNT-CNT conductance, the contribution of intrinsic conductivity of CNTs is found to control the value of the effective conductivity of CNT networks at densities and CNT lengths typical for real materials; (3) Several distinct regimes of the acoustic energy dissipation are established in atomistic simulations of individual CNTs; (4) The dominant role of bending buckling in stabilization of CNT networks is revealed and the contribution of the thermal resistance of buckling kinks to the thermal conductivity of CNT materials is established.

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Scaling laws and mesoscopic modeling of heat transfer in nanofibrous materials and composites

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Technical Abstract:

The structure – thermal transport properties relationship for nanofibrous materials based on carbon nanotubes (CNTs) are investigated by performing a multiscale computational study combining atomistic molecular dynamics simulations of heat transfer in small groups of CNTs with mesoscopic modeling of thermal conductivity in CNT-based materials, such as CNT bundles, "buckypaper," and vertically-aligned CNT "forests." Some of the key results of this study are as follows. (1) General scaling laws governing the heat transfer in nanofibrous network materials with different structures are derived analytically and verified in mesoscopic simulations; (2) Contrary to the common assumption of the dominant effect of the contact CNT-CNT conductance, the contribution of intrinsic conductivity of CNTs is found to control the value of the effective conductivity of CNT networks at densities and CNT lengths typical for real materials; (3) Several distinct regimes of the acoustic energy dissipation are established in atomistic simulations of individual CNTs; (4) The dominant role of bending buckling in stabilization of CNT networks is revealed and the contribution of the thermal resistance of buckling kinks to the thermal conductivity of CNT materials is established.

Publications:

1. L. V. Zhigilei, A. N. Volkov, E. Leveugle, and M. Tabetah, The effect of the target structure and composition on the ejection and transport of polymer molecules and carbon nanotubes in matrix-assisted pulsed laser evaporation, *Appl. Phys. A* **105**, 529-546, 2011.

2. A. N. Volkov and L. V. Zhigilei, Massively parallel mesoscopic simulations of gas permeability of thin films composed of carbon nanotubes, in *Computational Fluid Dynamics* 2010, A. Kuzmin (ed.), (Springer-Verlag, Berlin, Heidelberg, 2011), pp. 823-831.

3. A. N. Volkov, T. Shiga, D. Nicholson, J. Shiomi, and L. V. Zhigilei, Effect of bending buckling of carbon nanotubes on thermal conductivity of carbon nanotube materials, *J. Appl. Phys.* **111**, 053501, 2012.

4. L. V. Zhigilei, A. N. Volkov, and A. M. Dongare, Computational study of nanomaterials: From large-scale atomistic simulations to mesoscopic modeling, *Encyclopedia of Nanotechnology*, B. Bhushan (Ed.), (Springer, Heidelberg, 2012), Part 4, pp. 470-480.

5. A. N. Volkov and L. V. Zhigilei, Heat conduction in carbon nanotube materials: Strong effect of intrinsic thermal conductivity of carbon nanotubes, *Appl. Phys. Lett.* **101**, 043113, 2012.

6. W. M. Jacobs, D. A. Nicholson, H. Zemer, A. N. Volkov, and L. V. Zhigilei, Acoustic energy dissipation and thermalization in carbon nanotubes: Atomistic modeling and mesoscopic description, *Phys. Rev. B* **86**, 165414, 2012.

7. A. N. Volkov, R. N. Salaway, and L. V. Zhigilei, Atomistic simulations, mesoscopic modeling, and theoretical analysis of thermal conductivity of bundles composed of carbon nanotubes, *J. Appl. Phys.* **114**, 104301, 2013.

8. R. N. Salaway and L. V. Zhigilei, Molecular dynamics simulations of thermal conductivity of carbon nanotubes: Resolving the effects of computational parameters, *Int. J. Heat Mass Transfer*, in press, 2013.

9. A. N. Volkov and L. V. Zhigilei, Thermal conductivity of disordered fibrous materials governed by inter-fiber thermal contact conductance and intrinsic conductivity of fibers. I. Two-dimensional case, at the final stage of preparation for submission to *Phys. Rev. E*, 2014.

10. A. N. Volkov and L. V. Zhigilei, Thermal conductivity of disordered fibrous materials governed by inter-fiber thermal contact conductance and intrinsic conductivity of fibers. II. Three-dimensional case, at the final stage of preparation for submission to *Phys. Rev. E*, 2014.

Presentations:

(a) invited presentations by the PI

1. Multiscale (atomistic to mesoscopic) modeling of carbon nanotube materials, Seminar at the *Department of Chemistry, Clemson University*, Clemson, South Carolina, November 14, 2013.
2. Mesoscopic modeling of carbon nanotube materials: Computational model and applications to structural, thermal and mechanical properties, Symposium on "Innovations in Molecular Modeling: New tools and Applications," *ACS Southeastern Regional Meeting*, Raleigh, North Carolina, November 14-17, 2012.
3. The effect of the target structure and composition on the ejection of polymer molecules and carbon nanotubes in matrix-assisted pulsed laser evaporation: Molecular dynamics simulation study, *International High-Power Laser Ablation Conference*, Santa Fe, New Mexico, April 30 – May 3, 2012.
4. Mesoscopic modeling of collective dynamic phenomena in molecular systems and carbon nanotube materials, *Graduate Seminar at the Department of Materials Science and Engineering, University of Florida*, Gainesville, Florida, December 7th, 2011.
5. Multiscale (atomistic to mesoscopic) modeling of carbon nanotube materials, ACS Southeastern Regional Meeting, Richmond, Virginia, October 26-29, 2011.
6. Mesoscopic modeling of collective dynamic phenomena in molecular systems and carbon nanotube materials, *Core University Materials Genome Initiative Workshop*, Oak Ridge National Laboratory, October 26, 2011.
7. Multiscale (atomistic to mesoscopic) modeling of carbon nanotube materials, *American Physical Society March Meeting*, Dallas, Texas, March 21-25, 2011.

(b) contributed presentations

1. B. K. Wittmaack, A. N. Volkov, L. V. Zhigilei, Mesoscopic dynamic modeling of structural, thermal, and impact resistance properties of vertically aligned carbon nanotube (VACNT) forests, *MRS 2013 Fall Meeting*, Boston, Massachusetts, December 1-6, 2013.

2. R. N. Salaway, A. N. Volkov, L. V. Zhigilei, Molecular dynamics simulations of thermal transport in carbon nanotube structures: Effect of computational procedures and parameters, *2013 MRS Spring Meeting*, San Francisco, California, April 1-5, 2013.

3. R. N. Salaway, A. N. Volkov, L. V. Zhigilei, Structural factors affecting thermal transport in carbon nanotube materials, *2013 MRS Spring Meeting*, San Francisco, California, April 1-5, 2013.

4. R. Salaway, A. Volkov, and L. Zhigilei, Thermal conductance at carbon nanotube junctions and the effects of local structure (IMECE2012-89508), *ASME International Mechanical Engineering Congress and Exposition*, Houston, Texas, November 9-15, 2012.

5. R. Salaway, A. N. Volkov, and L. V. Zhigilei, Thermal Conductance at CNT-CNT Contacts: Influence of Contact Density and Local Structure (HT2012-58098), *ASME 2012 Summer Heat Transfer Conference*, Puerto Rico, USA, July 8-12, 2012.

6. A. N. Volkov and L. V. Zhigilei, Mesoscopic simulations and scaling laws of heat transfer in carbon nanotube materials: Effect of conductivity of individual nanotubes (HT2012-58102), *ASME 2012 Summer Heat Transfer Conference*, Puerto Rico, USA, July 8-12, 2012.

7. L. V. Zhigilei, A. N. Volkov, R. Salaway, W. M. Jacobs, D. A. Nicholson, H. Zemer, Computational study of thermal transport in carbon nanotube materials, *NSF 2012 CBET Grantee Conference*, Baltimore, Maryland, June 6-8, 2012.

8. R. Salaway, A. Volkov, and L. Zhigilei, Divergence in non-equilibrium molecular dynamics simulations of carbon nanotube conductivity and the effect of system parameters, *Pan-American Advanced Studies Institute on Computational Material Science for Energy Generation and Conversion*, Santiago, Chile, January 9-20, 2012.

9. R. Salaway, D. Nicholson, A. N. Volkov, L. V. Zhigilei, Thermal properties of carbon nanotubes and the effects of interacting neighbors, *ASME 2011 International Mechanical Engineering Congress & Exposition*, Denver, Colorado, November 11-17, 2011.

10. L. V. Zhigilei, A. N. Volkov, R. Salaway, D. Nicholson, and W. Jacobs, Thermal conductivity of carbon nanotube materials: Atomic-level simulations, mesoscopic modeling and scaling laws, *AFOSR Thermal Sciences Grantees' Meeting*, Arlington, Virginia, 26-28 September, 2011.

11. R. Salaway, A. N. Volkov, L. V. Zhigilei, Thermal conductivity of carbon nanotubes: The effect of inter-nanotube interactions, *AFOSR Thermal Sciences Grantees' Meeting*, Arlington, Virginia, 26-28 September, 2011.

12. L. V. Zhigilei, A. N. Volkov, W. Jacobs, D. Nicholson, and R. Salaway, Multiscale computational study of carbon nanotube materials, *2011 Joint Annual conference of the National Society of Black Physicists and National Society of Hispanic Physicists*, Austin, Texas, 21-24 September 2011.

13. A. N. Volkov, R. Salaway, D. Nicholson, W. Jacobs, L. V. Zhigilei, Thermal conductivity of carbon nanotube materials: Mesoscopic modeling and scaling laws, *Materials Research Society Spring Meeting*, San Francisco, California, April 25 - 29, 2011.

Summary of research findings and deliverables:

(1) In films, mats, buckypaper, and other materials composed of carbon nanotubes (CNTs), individual CNTs are bound together by van der Waals forces and form entangled networks of bundles. Mesoscopic dynamic simulations reproduce the spontaneous self-assembly of CNTs into continuous networks of bundles and reveal that bending buckling plays the dominant role in the generation and stabilization of the network structures. Bending buckling of CNTs reduces the bending energy of interconnections between bundles and stabilizes the interconnections by creating effective barriers for CNT sliding. In collaboration with a research group of Prof. Shiomi, University of Tokyo, Japan, the effect of bending buckling of carbon nanotubes on thermal conductivity of nanotube-based materials is investigated. Buckling kinks hamper phonon transport along the buckled nanotubes and serve as "thermal resistors" for the heat transfer along CNTs. Atomistic simulations reveal the dependence of the thermal conductance of a buckling kink on the buckling angle, whereas the mesoscopic simulations of thermal transport in "buckypaper" help to translate this information to the effective thermal conductivity of these complex network materials. The predictions of the simulations quantify an important factor that is responsible for the relatively low values of thermal conductivity of carbon nanotube materials reported in experimental studies.

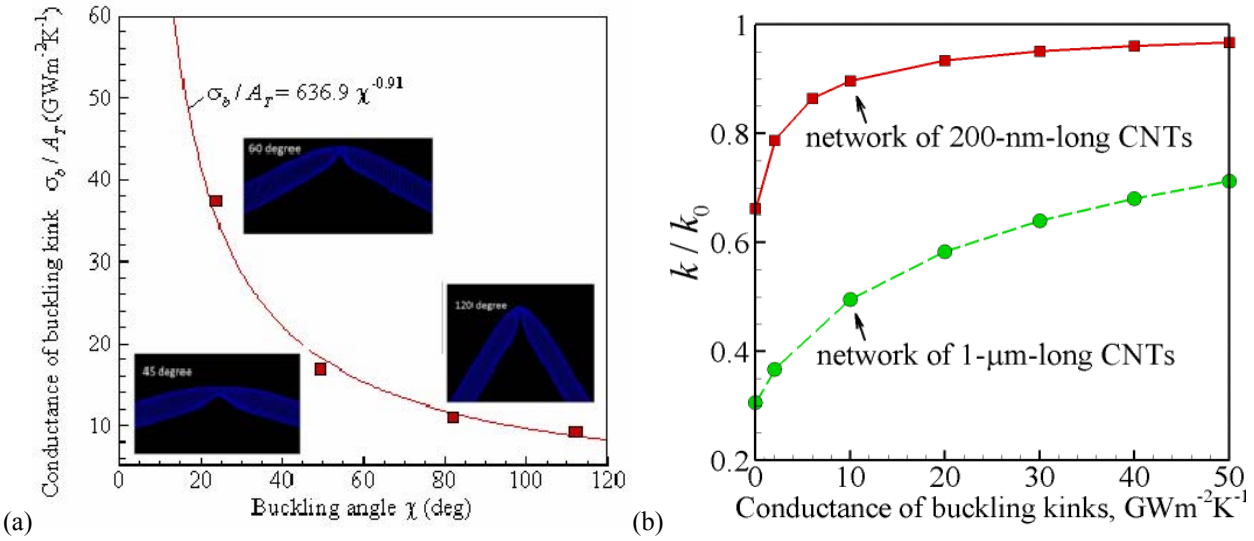


Figure 1. The dependence of the thermal conductance of the bending buckling kink on the buckling angle predicted for (10,10) CNTs in atomistic simulations (a) and the ratio of thermal conductivity k calculated for different values of constant conductance of buckling kinks to the thermal conductivity k_0 calculated with zero thermal resistance of buckling kinks. The results are shown for samples composed of CNTs with length of 200 nm (red squares & solid curve) and 1000 nm (green circle & dashed curve).

The results are reported in [A. N. Volkov, T. Shiga, D. Nicholson, J. Shiomi, and L. V. Zhigilei, *J. Appl. Phys.* **111**, 053501, 2012]

(2) Computational study of thermal conductivity of interconnected networks of bundles in carbon nanotube (CNT) films reveals a strong effect of the finite thermal conductivity k_T of individual nanotubes on the conductivity k of CNT materials. This effect is explained in a theoretical analysis that yields an analytical equation describing the effect of finite k_T on the value of k for different CNT materials:

$$k = \frac{k^0}{1 + \mathrm{Bi}_T / 12}$$

where k_0 is the conductivity at $k_T = \infty$, $\mathrm{Bi}_T = \sigma_c \langle N_J \rangle L_T / (k_T A_T)$ is the Biot number defined by the total contact conductance $\sigma_T = \sigma_c \langle N_J \rangle$ of a nanotube *at all contacts* it has with other CNTs, σ_c is CNT-CNT contact conductance, $\langle N_J \rangle$ is the averaged number of thermal contacts per CNT. Contrary to the common assumption of the dominant effect of the contact conductance, the contribution of the finite k_T is found to control the value of k at material densities and CNT lengths typical for real materials. The results are published in [A. N. Volkov and L. V. Zhigilei, *Appl. Phys. Lett.* **101**, 043113, 2012]

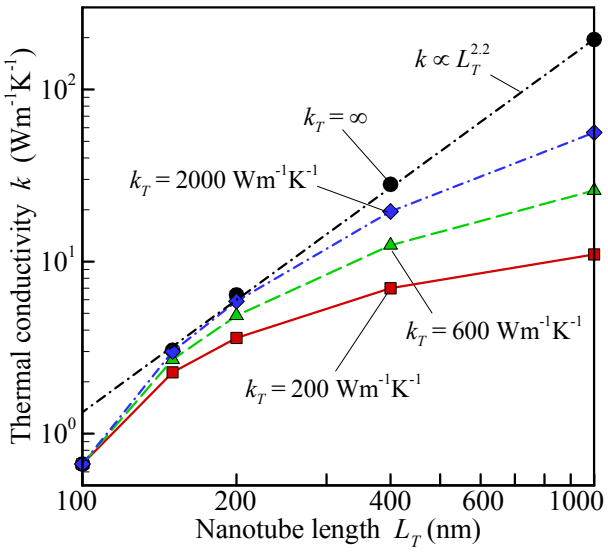


Figure 2. Thermal conductivity k of CNT films generated in mesoscopic simulations vs. nanotube length L_T for different values of the intrinsic thermal conductivity of CNTs, k_T. Dash-dotted black line is the power law fit to the values obtained for $k_T = \infty$.

(3) The exchange of energy between low-frequency mechanical oscillations and high-frequency vibrational modes in CNTs is investigated in a series of atomistic simulations. Several distinct regimes of energy dissipation, dependent on the initial stretching or bending deformations, are established. The onset of axial or bending buckling are found to induce the transition from a regime of slow thermalization to a regime in which the energy associated with longitudinal and bending oscillations is rapidly damped. The results of the atomistic simulations are used in the design and parameterization of a "heat bath" description of thermal energy in a mesoscopic model, which is capable of simulating systems consisting of thousands of interacting CNTs.

The results are published in [Jacobs et al., *Phys. Rev. B* **86**, 165414 (2012)]

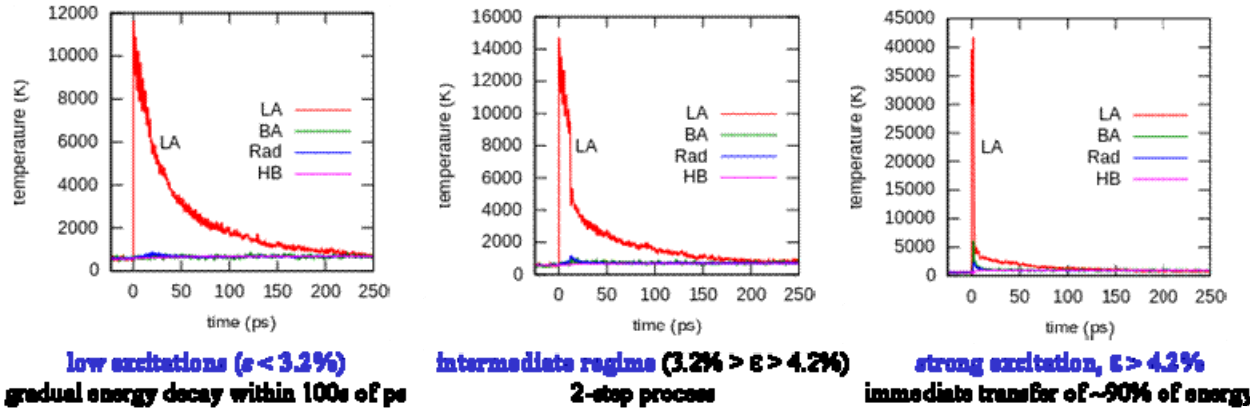


Figure 3. The evolution of energy of different groups of vibrational modes in MD simulation of CNTs with different levels of initial stretching deformation.

(4) Non-equilibrium MD simulations of heat transfer between adjacent CNTs and the intrinsic conductivity of CNTs in a bundle are performed for nanotubes of different length. The results of MD simulations suggest that, contrary to the widespread notion of strongly reduced conductivity of CNTs in bundles, van der Waals interactions between defect-free well-aligned CNTs in a bundle have negligible effect on the intrinsic conductivity of the CNTs. The simulations of inter-tube heat conduction performed for partially overlapping parallel CNTs indicate that the conductance through the overlap region is proportional to the length of the overlap.

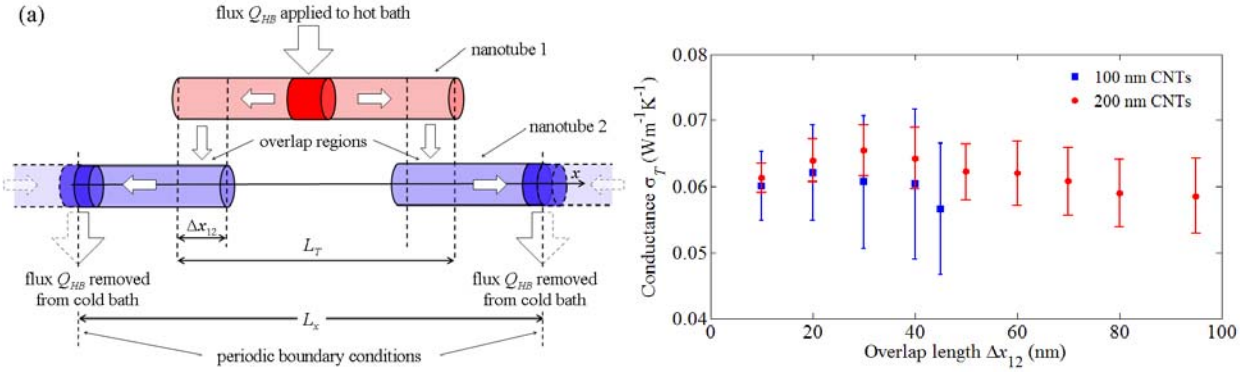
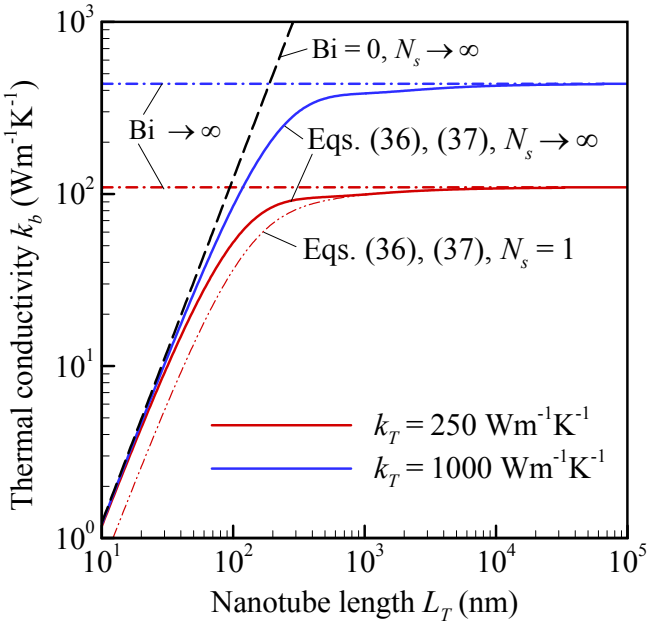


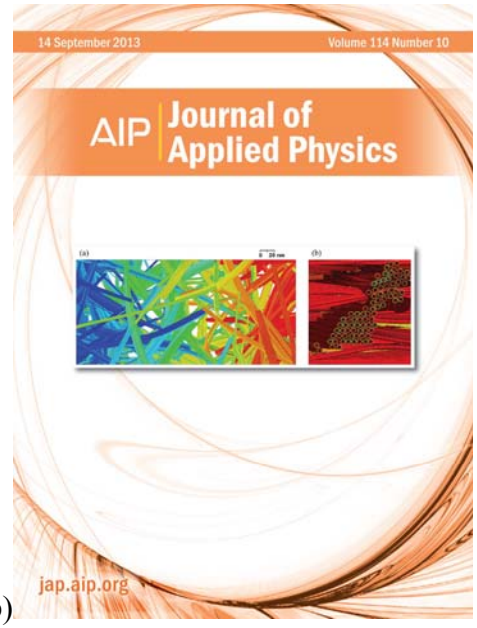
Figure 4. Schematic representation of the computational setup used in MD simulations of inter-tube heat conductance between two parallel partially overlapping (10,10) CNTs (a) and the dependence of inter-tube conductance per unit length on the overlap length predicted in the simulations of 100 nm (blue squares) and 200 nm (red circles) nanotubes. The results are reported in [A. N. Volkov, R. N. Salaway, and L. V. Zhigilei, *J. Appl. Phys.* **114**, 104301, 2013].

(5) The mechanisms and scaling laws governing the heat transfer within the primary building blocks of the network CNT structures – close-packed bundles of CNTs - are studied theoretically and in mesoscopic simulations. Based on the predictions of the MD simulations, a mesoscopic-level model is developed and applied for investigation of heat transfer in bundles consisting of CNTs with infinitely large and finite intrinsic thermal conductivity. The general scaling laws

predicting the quadratic dependence of the bundle conductivity on the length of individual CNTs in the case when the thermal transport is controlled by the inter-tube conductance and the independence of the CNT length in another limiting case when the intrinsic conductivity of CNTs plays the dominant role are derived. An application of the scaling laws to bundles of single-walled (10,10) CNTs reveals that the transition from inter-tube-conductance-dominated to intrinsic-conductivity-dominated thermal transport in CNT bundles occurs in a practically important range of CNT length from ~20 nm to ~40 μm.



(a)



(b)

Figure 5. Thermal conductivity of bundles of (10,10) CNTs calculated with analytical equations predicting the dependence of the bundle conductivity on the length of individual nanotubes, L_T, (a). The results are shown for two values of thermal conductivities of individual CNTs: k_T = 250 Wm^{-1}K^{-1} (red curves) and 1000 Wm^{-1}K^{-1} (blue curves). The results are reported in [A. N. Volkov, R. N. Salaway, and L. V. Zhigilei, *J. Appl. Phys.* **114**, 104301, 2013]. A figure from this paper is used for cover art for the journal issue (b).

(6) The mechanisms of material ejection in Matrix-Assisted Pulsed Laser Evaporation (MAPLE), an important technique used for deposition of thin polymer films and nanocomposite coatings, are investigated for targets composed of networks of nanotubes embedded into volatile solvent. The simulations demonstrate the ability of MAPLE technique to eject and transfer large structural elements that may be required for deposition of nanostructured films and coatings. The results are reported in [L. V. Zhigilei, A. N. Volkov, E. Leveugle, M. Tabetah, *Appl. Phys. A* **105**, 529, 2011] and illustrated in Fig. 6.

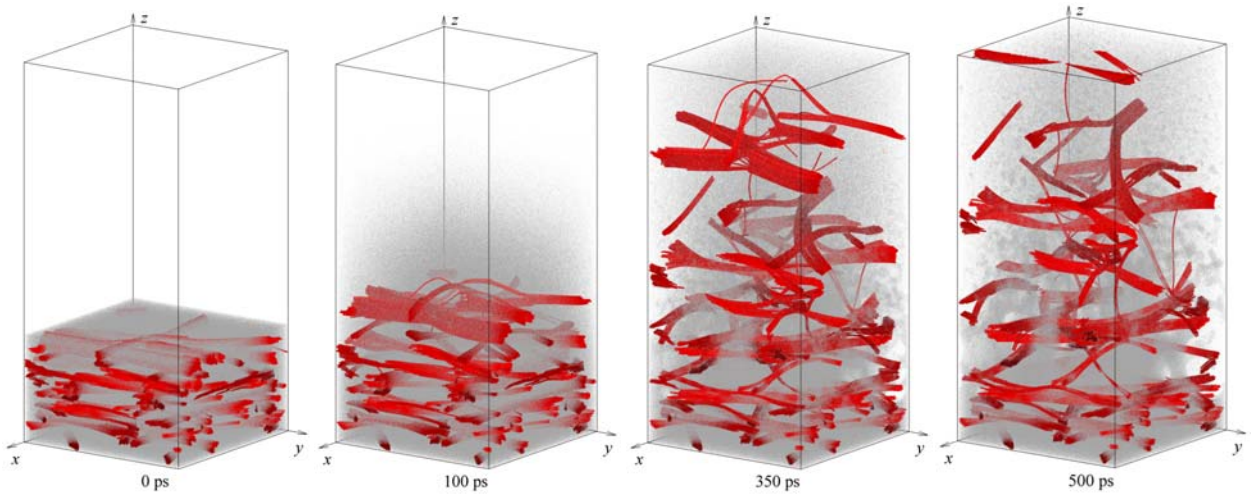


Figure 6. Snapshots of molecular configurations obtained in a large-scale simulation of the ejection of CNTs from a MAPLE target loaded with 17 wt.% of 150 nm long CNTs arranged into a network of bundles. The nanotubes are shown as red cylinders and the matrix molecules are shown as small gray dots.

(7) The mesoscopic model has been adopted for simulation of gas flow through CNT films. The results of the simulations suggest a moderate structural sensitivity of the gas diffusivity, with about 3–4.5 times lower values of self-diffusivity predicted for films with dispersed CNTs as compared to continuous network of CNT bundles (9% volume fraction of CNTs). [A. N. Volkov and L. V. Zhigilei, in *Computational Fluid Dynamics 2010*, A. Kuzmin (ed.), (Springer-Verlag, Berlin, Heidelberg, 2011), pp. 823-831].

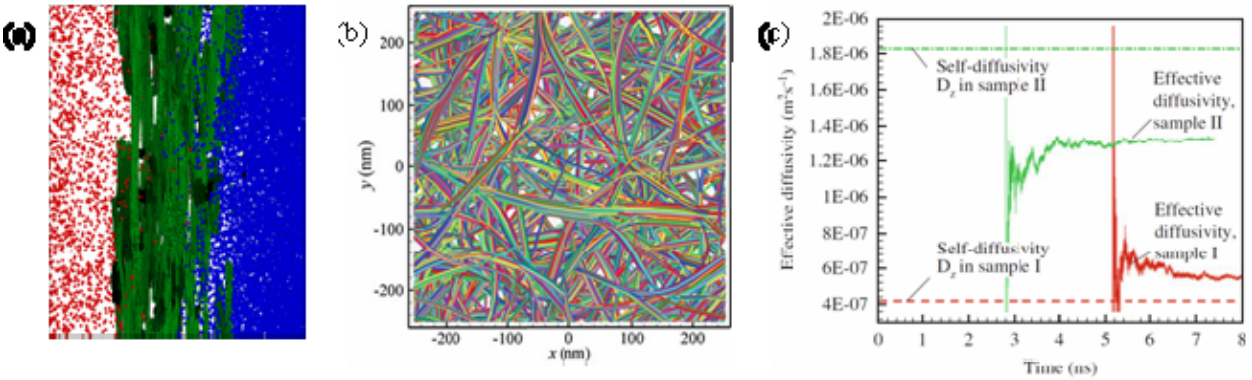


Figure 7. Snapshot from a simulation of the gas permeability in a film composed of CNTs (a), structure of the film used in the simulations (b), and the values of effective diffusivity vs. time in the gas permeation simulations (c).

(8) [current work - unpublished results] Computational methodology is developed for mesoscopic modeling of realistic structures of vertically aligned CNT (VACNT) structures. The structural properties of simulated VACNT "forests," e.g., Fig. 8, accurately reproduce those found in various experimentally grown VACNT materials. Structural dependence of thermal and mechanical properties of VACNT materials is currently investigated.

A series of simulations of nanoparticle impact on VACNT forests and CNT films are performed for a range of initial velocities and diameters of the projectiles. The mechanisms of the impact energy dissipation and the main channels of the energy propagation from the impact site are investigated in the simulations.

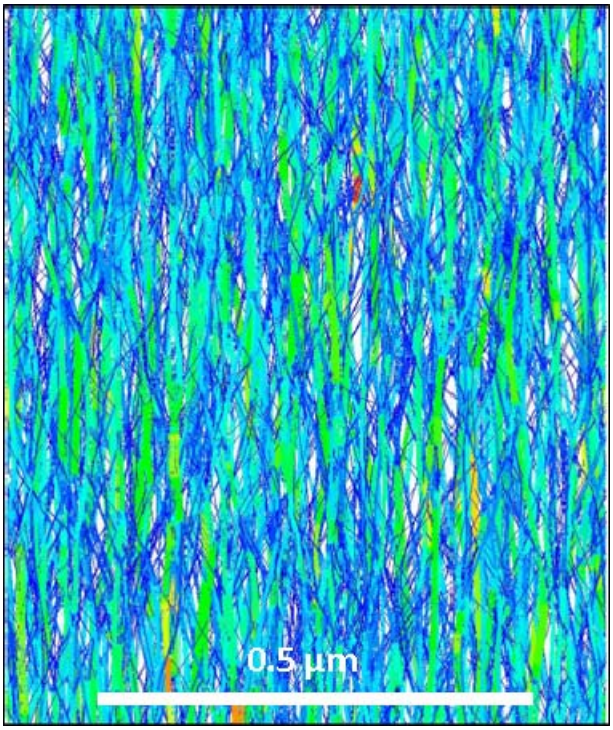


Figure 8. Structure of a CNT "forest" (vertically-aligned CNT array) with density 0.02 g/cm^3. The model material is composed of 2 μm long (10,10) CNTs. The color shows the local thickness of bundles in the material.

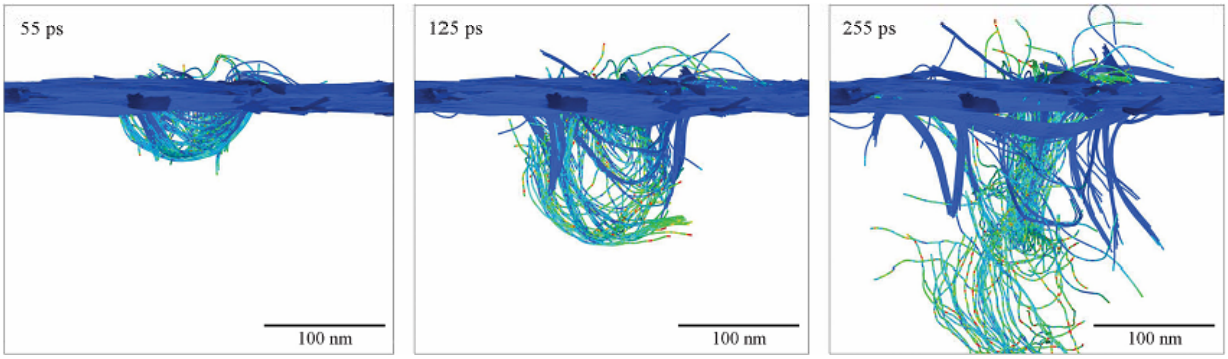


Figure 9. Snapshots from a mesoscopic simulation of the high-velocity impact of a spherical projectile with a diameter of 100 nm, a density of 2.8 g/cm^3 and an initial velocity of 1000 m/s on a free-standing 20-nm-thick CNT film. The film has a density of 0.2 g/cm^3, and the CNTs in the film are arranged in a continuous network of bundles. The nanotubes are colored by their local kinetic energy, and the projectile is not shown in the snapshots.